SEA WATER CONVERSION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

"Study of Permeability Characteristics of Membranes"

Annual Report

Covering Period

November 9, 1967 - November 9, 1968

K. S. Spiegler, Principal Investigator
J. C. Th. Kwak
D. A. Zelman
J. Leibovitz (part time)

Contract No. 952109
Jet Propulsion Laboratory
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TABLE OF CONTENTS

ABSTRACT

A novel apparatus for the measurement of all membrane transport properties under the influence of electrical, osmotic and pressure force is reported. This apparatus was built with a view to (a) measure all transport properties under the same conditions of concentration and of solution agitation and (b) incorporate suitable feedback mechanisms so as to keep the solution concentration throughout the measurement constant in spite of the mass transfer which takes place.

Transport is not measured by the difference of solution concentrations before and after the transport experiment, as customary, but rather by the amounts of the components added to the solutions (water or salt) by these feedback mechanisms.

Since temperature and concentration control within very narrow limits is maintained, a detailed description of the feedback and control devices used is presented in this report. The performance of temperature regulation and concentration feedback mechanism is reported and found to be adequate for most measurements.

A set of experiments is outlined, based on transport parameter evaluation from the basic flux equations of linear non-equilibrium thermodynamics or on a transformed set of equations as developed by Duncan. Results of some preliminary transport experiments are given.

I. INTRODUCTION

I-1. Theoretical Considerations

This is the first annual report of a research program designed to construct one apparatus in which transport of salt, ions and water across membranes can be determined with differences in chemical potential, electric potential and pressure as driving forces, together with the measurement of membrane and streaming potential. This will permit us to study the performance of separators and membranes from a minimum of basic characterization measurements.

Many membrane transport properties have been measured by various authors for synthetic membranes. Reviews of this work are written by Helfferich[1] and Lakshminarayanaiah[2]. In recent studies several investigators have used the A.M.F. C-103 (American Machine & Foundry Co., Springdale, Conn.) cation exchange membrane[3,4,5,6] for transport measurements. Their results indicate that this commercially available membrane is very suitable for performing consistent and reproducible transport measurements. Our cell design is based on the transport properties of this membrane that were available from literature data.

A system of phenomenological coefficients derived from irreversible thermodynamic theory will be used for expressing the various transport properties. Since these phenomenological coefficients are often strongly dependent on the salt concentration, it is important to keep the concentration profile across the membrane constant. Experimentally one can maintain the concentrations in the two solutions at either side of the membrane constant. Also, in order to decrease the influence of the boundary layers

between membrane and solution it is important to have effective stirring near the membrane and to do all experiments in the same cell under the same hydrodynamic conditions. Special emphasis therefore has been given to design a cell in which all the transport parameters can be measured by interchanging various parts of the cell, without changing the geometrical arrangement near the membrane. The initial experiments have been carried out with aqueous NaCl solutions of different concentration on either side of the membrane.

Staverman[7] first applied irreversible thermodynamics to membrane transport processes and showed that as a first approximation the fluxes J_+, J_- and J_w are proportional to the driving forces (subscripts +, -, and w refer to Na^+, Cl^- and water respectively):

$$J_i = - \sum_{i,j} L_{ij} \, \partial \tilde{\mu}_j / \partial x \qquad (1)$$

where $\tilde{\mu}_i$ is the electrochemical potential of species i:

$$d\tilde{\mu}_j = d\mu_j^c + \bar{v}_j \, dp + \mathcal{F} z_j \, d\phi \qquad (2)$$

x is the length coordinate direction perpendicular to the membrane. The approximations involved in assuming a linear relation between J_i and the gradients of the total electrochemical potentials $\tilde{\mu}_j$ as expressed by equation (1) are numerous. They include the assumption that the system is close to equilibrium, so that the $\tilde{\mu}_j$ may be obtained from equilibrium functions. Also the time scale of relaxation of the system should be large compared to the molecular relaxation time. It is very difficult to estimate from first principles when this linearity will break down and an experimental approach is necessary to determine the dependence of the coefficients L_{ij} on the magnitude of the driving forces. However, classical linear

relations e.g. Kohlrausch's and D'Arcy's law give hope that the L coefficients are independent of electric potential and pressure. On the other hand in aqueous solutions the L_{ij} turn out to be strongly concentration-dependent[8], and substantial concentration-dependence is expected in membranes also in view of the considerable variation of co-ion concentration profile in the membrane with the concentrations of the terminal solutions (ref. 1, Chapter 8).

Several authors transform the fluxes in equation (1) to fluxes of the salt J_s, water, J_w, and the electric current density, i, with the gradients in the concentration-dependent part of the chemical potential, the pressure and the electric potential[9,10,11] as driving forces. The resulting new phenomenological coefficients can be calculated directly from the experimental results and then transformed to the original L coefficients. Duncan[12] transformed equation (1) to a system in which the volume flux, the "salt-water separation flux" and the membrane potential are linearly expressed in terms of the pressure difference, concentration difference and electric current density. His relations are especially useful to relate the measured quantities directly to a system of practical phenomenological coefficients for which Onsager's relation holds. The derivation of his equations is given in the appendix.

A different approach to relate the forces and fluxes appearing in the entropy production is known as the friction coefficient formalism[13,14,15,16]:

$$\partial\tilde{\mu}_j/\partial x = \sum_j X_{ij} (v_i - v_j) \qquad (3)$$

It should be remarked that the authors mentioned, although essentially using the same formalism, each define their set of "friction coefficients" in a slightly different way. Equation (3) is the one used by Spiegler[15] and

his X_{ij} can easily be converted into the coefficients used by the other authors. In electrolyte solutions these "friction coefficients" X_{ij} are much less concentration dependent than the admittance coefficients L_{ij}. Further, they are not dependent on the reference velocity, as the L coefficients are. Therefore, their suitability for tabulating and comparing data for various membranes surpasses other phenomenological fomulations.

When the approximation is made that the coion-counterion friction interaction is negligible, the friction coefficients can be calculated from a smaller number of measurements, than are theoretically necessary. In any event, the admittance coefficients L_{ij} can be expressed in terms of the friction coefficients and the concentrations of the mobile species in the membrane[15]. We plan to express our results in both admittance and friction coefficients and try to determine to what degree the coefficients are influenced by concentration and concentration differences.

In order to make sure that our measurements can give useful information and represent the properties of the membrane alone, the experimental design was designed to satisfy the following requirements:

1) The concentrations in the compartments at either side of the membrane are the same for all measurements defining a single set of coefficients.
2) The concentrations in each compartment do not change during a transport experiment.
3) The mass-transfer resistance of the two membrane-solution interfaces should be as small as possible.
4) The hydrodynamic situation in the bulk electrolyte near the membrane should be similar in all measurements.

A practical difficulty is that a change of the driving force essentially

results in a change of state of the system. Due to this change of state even the friction coefficients may change with the forces. Also the boundary layer and even the membrane itself are in principle in a different state in different experiments. (This difficulty is inherent in all transport correlation work in membranes. In our work we attempt to minimize it by the special experimental conditions chosen.) Thus the question arises whether one can at all justify comparing the phenomenological coefficients at different driving forces. On the other hand, the presence of concentration, potential and pressure differences is essential for performing the various transport experiments. By satisfying requirements 1-4 we may hope to maintain at least the concentration profiles in the membrane as similar as possible in the different experiments, so that a consistent and meaningful set of L_{ij} or X_{ij} coefficients can be calculated from the measured flows and potentials. Conditions 1 and 2 are necessary because of the concentration-dependence of the transport coefficients. By keeping all concentrations constant while actual transport takes place the L coefficients for fixed terminal concentrations can be obtained instead of an average value over terminal concentrations changing during the measurements. The important influence of the membrane-solution boundary layers on the measurement of membrane transport properties is seen from the work of Scattergood and Lightfoot[5], Kaufmann and Leonard[17] and Litt and Smith[18]. However, the work of these authors also shows that by controlled stirring these boundary layer effects may be evaluated and extrapolation to the real membrane transport coefficients can be made.

I-2. Principles of Measurement

It is seen from equation (2) that in an isothermal system solution 1-membrane-solution 2 the three driving forces for transport that can be

applied are gradients of pressure, concentration part of the chemical potential and electric potential. However, the experimentally independent parameters are the differences in these quantities from one compartment to the other, Δp, $\Delta \mu^c$ and $\Delta \phi$ (or the total electric current I). Equation (1) can be integrated to yield these differences rather than the gradients. Let us now consider the following system:

$$\mathrm{Ag}\,|\,\mathrm{AgCl} \quad \begin{matrix}\mathrm{NaCl}^{1}\ (\mathrm{C}') \\ \mathrm{H_2O}\end{matrix} \quad \Big| \quad \begin{matrix}\mathrm{NaCl}^{2}\ (\mathrm{C}'') \\ \mathrm{H_2O}\end{matrix} \quad \mathrm{AgCl}\,|\,\mathrm{Ag}$$

In this system the following experiments can be performed, thus satisfying conditions 1 and 2 of Section I-1, leaving Δp and i as the remaining independent parameters:

1) Osmosis↔dialysis experiment. $\Delta p=o$, $i=o$, Δc finite. Measure salt flux $(J_s)_{i,\Delta p=o}$, volume flux $(J_v)_{i,\Delta p=o}$ and membrane potential $(\Delta\phi_-)_{i,\Delta p=o}$. Dialysis coefficient = $(J_s)_{i,\Delta p=o} \cdot \frac{d}{c' - c''}$, osmotic permeability coefficient = $(J_v)_{i,\Delta p=o} \cdot \frac{1}{\pi' - \pi''}$.

2) Hyperfiltration experiment. $i=o$, Δp and Δc finite. Measure $(J_s)_{i=o}$, $(J_v)_{i=o}$ and $(\Delta\phi_-)_{i=o}$. Salt filtration coefficient = $[(J_s)_{i=o} - (J_s)_{i,\Delta p=o}] \cdot \frac{1}{\Delta p}$. Streaming potential = $(\Delta\phi_-)_{i=o} - (\Delta\phi_-)_{i,\Delta p=o}$. Here these coefficients are not defined for zero concentration difference, as usual.

3) Electromigration↔electroosmosis experiment. $\Delta p=o$, i, Δc finite. When a current is passed through the cell from electrode 1 (+) to electrode 2 (-) it is clear that for an ideally selective anion exchange membrane no concentration changes would occur. Thus the change in concentration indicating an apparent salt flux $(J_s)_{\Delta p=o}$ in fact is caused by Na^+ transport through the membrane. Then

the transference number of the Na^+ ion is given by: $t_{Na+} = [(J_s)_{\Delta p=o} - (J_s)_{i,\Delta p=o}] \cdot \frac{\mathcal{F}}{i}$ also $t_{H_2O} = [(J_v)_{\Delta p=o} - (J_v)_{i,\Delta p=o}] \cdot \frac{\mathcal{F}}{18i}$.

4) Conductivity experiment. $\Delta p=o$, i and Δc finite. D.C. conductivity measure $\Delta\phi$ and i. A.C. conductivity measure resistance directly in a bridge circuit.

These coefficients can easily be corrected for the small difference between water and volume transport. We then see that in total nine measurements have to be performed, defining independent coefficients of which six are related by the Onsager reciprocity relations.

In order to maintain the concentration profile in the membrane invariant, no concentration changes should occur in each cell compartment during the actual transport measurement. This means that a system had to be devised in which J_{H_2O} and J_s can be measured without relying on the usual method of detecting the concentration changes with regard to time. Therefore a concentration feedback system was constructed that keeps the concentration in either cell half very accurately constant. A detailed description of the system and its performance is given in Section II-3, here we present the principles of the method so as to be able to set up the equations from which the salt and volume flow in our experiments can be calculated.

At both sides of the membrane a conductivity cell is inserted in the system shown on page 11. The resistance of the cell solution is compared to that of a reference resistance by a very accurate impedance comparator (General Radio 1605-AH). The output of this comparator, which can be positive, negative or zero and which is metered with a full scale range of 0.1% difference, is amplified with a phase-sensitive amplifier to open or close a relay. At the depleted side this relay activates a Menisco Matic automatic buret (American Instrument Co., Silver Spring, Maryland) which

pushes a concentrated NaCl solution into the system until the reference resistance is reached again. In the salt-enriched compartment the relay actuates a sealed centrifugal pump (Model 7004-1, Cole Parmer, Chicago, Illinois 60648) which circulates the cell solution through an ion-exchange column. The pump stops when the column has taken up enough salt to lower the cell resistance to that of the reference resistance. When no pH changes due to electrode reactions or H_2O dissociation at the membrane occur, this system keeps the concentration at either side of the membrane constant with 0.02%. Then the salt flow can be calculated by measuring the volume pushed into the system by the buret $-\Delta v_b$, corrected for the volume change Δv_{app} at that side during the experiment:

$$J_s \cdot A \cdot t = - \Delta v_b \cdot c_b - \Delta v_{1,app} \cdot c' \qquad (4)$$

where c_b is the salt concentration in the buret solution, $\Delta v_{1,app}$ the volume change measured in a pipet connected to compartment 1 during an experiment and c' the concentration at the donating side of the membrane. At this side, the volume change due to the membrane transport process is given by:

$$J_v \cdot A \cdot t = - (\Delta v_{1,app} - f\Delta v_b - \Delta v_e) \qquad (5)$$

where f is a correction factor allowing for the volume change when the buret solution is mixed with the system solution and Δv_e is the volume change due to the electrode reaction in an experiment where current is passed. At the enriched side of the membrane the salt flux is given by:

$$J_s \cdot A \cdot t = n_{I.E.} + \Delta v_{2,app} \cdot c'' \qquad (6)$$

with $n_{I.E.}$ the number of moles taken up by the ion exchange column (to be analyzed when the experiment is completed), and c'' the concentration at this side of the membrane. At this side the volume flow can be calculated from:

$$J_v \cdot A \cdot t = \Delta v_{2,app} - g \cdot n_{I.E.} - \Delta v_e \qquad (7)$$

g is a correction factor describing the volume change of the ion exchange

resin when salt is taken up. Narrow temperature control in each cell half is extremely important for the performance of this feedback system. In Section II-2 the temperature control system is described as it was finally conceived.

When a current is passed through the cell large Ag/AgCl electrodes are used as working electrodes. However for measuring membrane and streaming potential small Ag/AgCl electrodes were constructed and will be inserted in each cell half.

No membrane conductivity measurements have been carried out yet, but the cell was designed so as to make them possible. Two methods can be used. In the normal A.C. method two large Pt electrodes are inserted in each cell half. By measuring the resistance with and without the membrane inserted the membrane resistance can be calculated. In our cell these electrodes are movable so that by varying the electrode distance and plotting the total resistance versus the electrode distance, two parallel straight lines should be obtained for the measurements with and without the membrane inserted. The resistance difference between these two lines at each electrode distance is the membrane resistance. Of course the method of measuring with and without membrane can not be used when there are different concentrations in each cell half. Then an extrapolation to zero distance has to be used.

II. Experimental

II-1. Membrane Transport Cell

II-1-1. Transport Cell

The transport cell (Figure 1) used for all measurements, is a cylindrical two compartment cell and consists of interchangeable cylinders and end parts, clamped together by two supporting steel plates and steel rods. Buna N O-rings are used as seals between the various parts. All parts were machined of "Lexan" (General Electric Co. tradename), a transparent polycarbonate plastic (West Lake Plastics, Lenni Mills, Pa.). The cylinders have an outer diameter of 4.5" and an inner diameter of 2". The end parts also have a diameter of 4.5" and are 1-1/8" thick.

The cell arrangement in Figure 1 is suitable for an electromigration↔ electroosmosis experiment. The end part of each compartment contains a mounting hole in which the Ag/AgCl working electrode (described in Section II-1-3) can be inserted. Two other 1/4" holes are made for connecting the cooling coils (Section II-2-3) to the outside. The cylinder next to the end part has the connections for the pipet, the inlet and outlet for the concentration feedback system, and the conductivity cell. All holes are 7/16"-20 N.F. (National Fine, i.e. straight thread) for standard "Swagelok" (Crawford Fitting Co., Solon, Ohio 44139) connectors, except the hole for the conductivity cell which is 3/4"-16 N.F. (Section II-1-2). At the inside of the cylinder 1/2" wide x 5/16" deep grooves are made for the cooling coil. In the next cylinder, provisions are made for accommodating a resistance thermometer, a Ag/AgCl measuring electrode((Section II-1-3) and a magnetic stirrer. The thermistor and the Ag/AgCl electrode are epoxy-sealed in "Zytel" "Swagelok" connectors, 3/8" tube o.d. for 9/16"-18 N.F. holes. All "Swagelok" connectors have an O-ring seal. The stirrer is a "Teflon"-

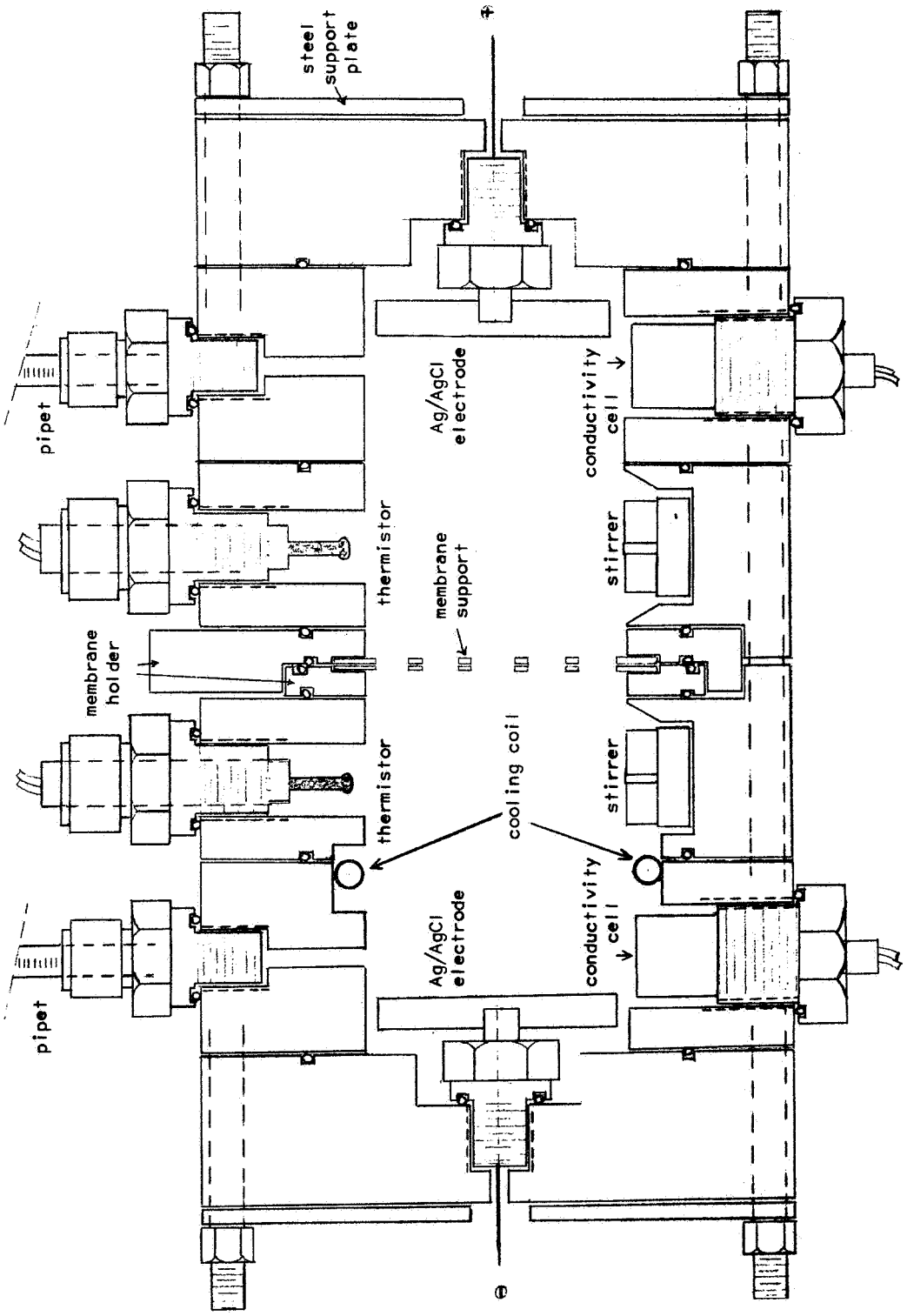

Figure 1.

Cell for Measurement of Transport Across Membranes

enclosed magnet and has the form of a 1/4" high fin on top of a 3/8" high cylinder, 3/4" diameter (Bel Art, Pequannock, N.J.). A cone was made in the bottom of the cell cylinder, leading to a 7/8" wide 1/4" deep cylindrical hole that keeps the stirrer in place. The stirrers are driven by two circular shaped, double pole magnets, 1" diameter, each mounted on a shaft which is held in place by a brass sleeve-bearing. The two shafts are connected with a pulley and one of them is driven by a A.C.-D.C. motor with a G.T. 21 variable speed control (Gerald K. Heller Company, Las Vegas, Nev.). This whole assembly is mounted solidly on an aluminum bracket and can easily be positioned underneath the cell. Stirring speeds up to 1500 rpm are reached; at higher speeds the stirrers do not follow the magnets. By using still stronger magnets this speed may be increased even more.

The membrane holder can be slid out of the cell without disassembling the other parts completely. The membrane is sealed by an O-ring at each side. The two parts of the membrane holder fit together tightly, and a soft rubber gasket is inserted between the left side stirring compartment and the membrane holder. With this design, we expect no evaporation from the membrane edges. Two 1/16" thick membrane supports can be inserted in the membrane holder. They are made of glass fiber-reinforced plastic, each one having 19 holes of 5/16" diameter. This reduces the membrane area from 20.3 cm^2 to 14.6 cm^2. When necessary, different supports can be made and inserted.

For membrane resistance measurements, a different end part than the one shown in Figure 1 is used. This part has a 3/8" hole into which the shaft of the conductivity electrode (Section II-1-4) can be fitted. Two O-rings are inserted in the 3/8" hole, spaced at 7/8", to seal the shaft.

The distance between the electrodes can be changed and measured by means of an adjusting screw pushing against the electrode shaft.

II-1-2. Conductivity Cells

The sensors for the concentration feedback systems are the conductivity cells shown in Figure 2. They are made of "Lexan". Platinized platinum electrodes are glued to the sides of the 1/2" long x 3/16" wide x 3/8" deep hole and are connected to a Pt wire leading to the outside via a 1/32" hole.

The threaded electrode holder fits into a 3/4"-16 N.F. threaded hole in the cylinder, O-ring sealed at the outside. Cell constants are between 2 and 10.

II-1-3. Ag/AgCl Electrodes

Ag/AgCl working electrodes, to be used in the electromigration↔ electroosmosis experiments, were constructed. A strip of silver metal, about 25" long, 1/4" wide, and 0.022" thick is wound as a spiral of 1-3/4" diameter (outer circumference). The spiral is mounted on a cylindrical "Lexan" plate, also 1-3/4" diameter and 1/4" thick. This assembly is mounted on a "Swagelok" hose connector, 1/4" hose diameter, 7/16"-20 N.F. thread, which can easily be inserted in the end part of the transport cell (Figure 1). A silver wire is welded to the silver strip and is sealed with epoxy inside the "Swagelok".

Seventy mmoles silver are deposited on the silver spiral out of a $KAg(CN)_2$ (10 gram/liter) solution. Then about 35 mmoles are converted to AgCl by electrolysis in a 0.1N HCl solution. By keeping the current density low (<1 ma/cm^2) and stirring well it seems that the whole surface area (approximately 70 cm^2) is covered quite uniformly. During an electromigration↔ electroosmosis experiment about 10 mmole of AgCl will be produced or consumed.

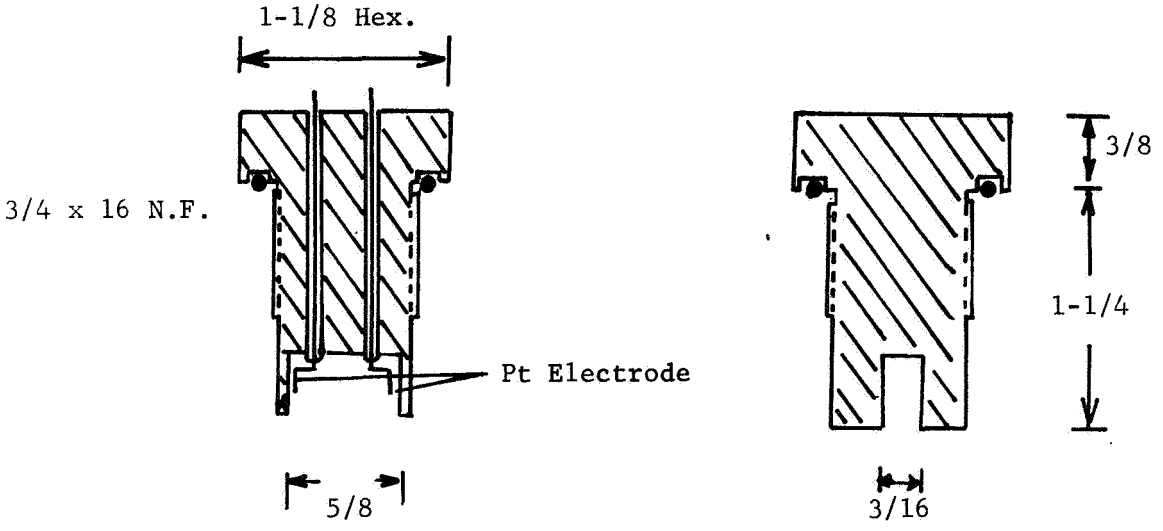

Figure 2.

Conductivity Cell

Material: Lexan

Dimensions are in inches.

The Ag/AgCl potential-measuring electrodes fit into a "Swagelok" connector that can be inserted in the section of the transport cell containing the stirrer. The electrode consists of a silver wire sealed with epoxy into a 1/4" glass tube that on one end is drawn into a capillary. The tip of the wire is first plated with silver and then chloridized. Asymmetry potentials of these simple electrodes are smaller than 0.1 mV.

II-1-4. Conductivity Electrodes

The A.C. resistance of the system solution 1 - membrane - solution 2 will be measured, and by varying the electrode distance, the resistance of the membrane can be determined. The circular electrodes consist of 0.004" platinum foil glued with "Plio-Bond" (Goodyear Tire & Rubber Co., Akron, Ohio) to a "Lexan" plate, 1-7/8" diameter. A platinum wire is welded to the foil and leads to the outside connection through a hollow rod mounted on the disc, perpendicular to its face. This rod is made of "Delrin" (E. I. duPont de Nemours Co., Wilmington, Delaware), a reinforced "Teflon" material, chosen for its strength and low friction. Each of the two assemblies consisting of electrode and rod is introduced into the end part of the cell through a double O-ring seal and can be moved forward and backward by means of an adjusting screw.

II-2. The Temperature Control System

II-2-1. Experimental Errors Caused by Temperature Effects

The cell temperature can not be adequately controlled by immersing the whole system in a constant temperature bath, because the heat dissipation in the cell from stirring and D.C. passage is usually too large to be transfered through "Lexan" to an air or liquid thermostat. Moreover, the many connections to the concentration feedback system, pipets, thermistors etc.

and the presence of the magnetic stirrers further complicate immersion in a liquid bath. Therefore it was decided to regulate the temperature in each cell half internally by introducing cooling coils into the cell and measuring the temperature inside each cell half, in addition to the location of the whole apparatus in a constant-temperature air bath. Narrow control and accurate measurement of the temperature are necessary for the following reasons:

1) Measurement of volume flow. In a preliminary dialysis experiment (c'(NaCl) = 0.2N, c''(NaCl) = 0.05N) a volume flow of about 0.5 ml per day was calculated from the apparent volume change in the pipet. If we require a thermal expansion-contraction error of less than 1%, this means that the temperature has to be regulated better than 0.1 °C [volume of cell compartment 200 ml, water expansion coefficient 0.2×10^{-3} ($°C^{-1}$)] and the differential measurement should be even better. Of course for smaller volume flows a higher accuracy is required.

2) Measurement of salt flow. Again in this preliminary dialysis experiment a salt flow of 0.12 mmole per day took place as calculated from the experimental data. However, since the concentration in each cell half is kept constant with the feedback mechanism and the concentration sensor for this is a conductivity cell, this constancy depends to a large extent on the temperature control. If we assume a temperature dependence of the conductance, κ, of 2% per °C, and again an accuracy in J_s of 1% is required, for cell half 1 [C (NaCl) = 0.2N, volume 200 ml] a differential temperature measurement of 1.5×10^{-3} °C is required. It is seen that for this

measurement the low concentration side is less influenced by temperature changes. In a typical electrodialysis experiment about 10 mmole per day will be transported and then less strict requirements are imposed temperature constancy and measurement. On the other hand, the measurement of the salt filtration coefficient will be influenced even more than the dialysis coefficient, unless each measurement is carried out over a period of several days in order to transfer reasonably large amounts of salt and water. From these examples it is seen that very accurate measurements and narrow control of the temperature in each cell half are essential for the accuracy of the measurements of salt and volume flow. The heating of the two solutions, due to stirrers and electric current, may account for appreciable temperature differences between the solutions and the environment. Therefore the temperature has to be measured and regulated inside each cell compartment individually.

II-2-2. Temperature Measurements

Thermistors, (47 A 13, Victory Engineering Corporation, Springfield, New Jersey, 07081) are used for measuring the temperature inside the cell. They are of the glass rod type, 0.1" diameter and 1 1/2" long and are sealed with epoxy in a 3/8" diameter tube, which can be inserted in a "Swagelok" straight-thread connector 600-1-OR. When the "Swagelok" connector is fitted into the cell, the tip of the thermistor is flush with the cell compartment (see Figure 1). The thermistors have a resistance of about 75,000 Ohm at 25 °C each and a temperature coefficient of -4.6% per °C. In still water they have a time constant of 1 second and a dissipation constant 5 mW/°C. This means that with a bridge excitation voltage of

4 volt D.C. the self heating (in well stirred water) will be less than 0.04 °C. This self heating is rather constant in time and does not influence our differential temperature measurements.

A double Wheatstone bridge was constructed for measuring the thermistor resistances. Variable D.C. excitation is used. The thermistors were calibrated against an accurate thermometer (Brooklyn Thermometer Company, Farmingdale, New York, 11735) to 0.01 °C between 24.5 and 25.5 °C, with a bridge excitation voltage of 4 volt D.C. Different series of calibrations showed repeatabilities of about 0.01 °C. Although these glass imbedded thermistors are stable in time, the calibrations will be repeated regularly. Of course a long term resistance instability would not influence the differential temperature measurement during an experiment.

The bridge output is measured on a Kintel 203A electrometer-amplifier (Cohu Electronics, Kintel Div., San Diego, Calif. 92112). A temperature change of 0.01°C causes a bridge imbalance of about 1 mV. Temperature differences of 0.002°C can be detected. During an experiment a 1 V full scale recorder is connected to the output of the Kintel electrometer.

II-2-3. Temperature Regulation

The temperature regulation consists of several steps. First the laboratory room temperature is regulated at 20 $\pm$ 1 °C. In this room a large box was built which contains the transport cell and some axilliary equipment. The cell is positioned in front of a large "Plexiglass" window in the side of the box. A fan is mounted at one side of the box and is driven by an electric motor at the outside. A thermistor in the middle of the box is connected to a Y.S.I. Thermistemp, Model 63, temperature controller (Yellow Springs Instrument Co., Yellow Springs, Ohio). The relay of

this controller shuts on or off 37% of the total heating power in the box. The total power of the heater (four 100 W light bulbs mounted in front of the fan) is provided by a variable transformer. The maximum output of this transformer can be varied by a clock motor which will decrease the output voltage when the controller signal is "on" and increase it when the signal is on "off". The coupling between the transformer and the clock motor provides for a 2 minutes delay between any upward and downward adjustment. In this way an automatic variation of the transformer setting is obtained as the demands of the system may vary due to ambient conditions.

This system provides for a constancy of the air temperature in the box of $\pm$ 0.1 °C over long periods. The on-off cycle of the controller is normally around 30 seconds. The temperature of the box is kept at 25.0 $\pm$ 0.1 °C.

The next step in our temperature regulation system is inside the cell. The heat dissipated inside the cell by the stirrer (and the electric current in electric transference experiments) has to be removed to keep the temperature constant at the desired level. Therefore cooling coils are inserted in grooves in the inside wall of the cell. The coils are made of copper tube, 1/4" o.d. and have a total length inside each cell half of 18 cm. They are introduced through "Swagelok" connectors in the end parts of the cell. A 1/2" wide x 5/16" deep groove at the inside of the cylinder next to the end part leads to a 270° circular groove at the inside of the stirrer compartment. In this way the surface of the coil is exposed directly to the solution without forming an obstacle for the current passing between the working electrodes. The outer surface of the coils is coated with a thin epoxy layer (Araldite, Ciba Products Company, Summit, New Jersey) to prevent corrosion and distortion of the electric current lines.

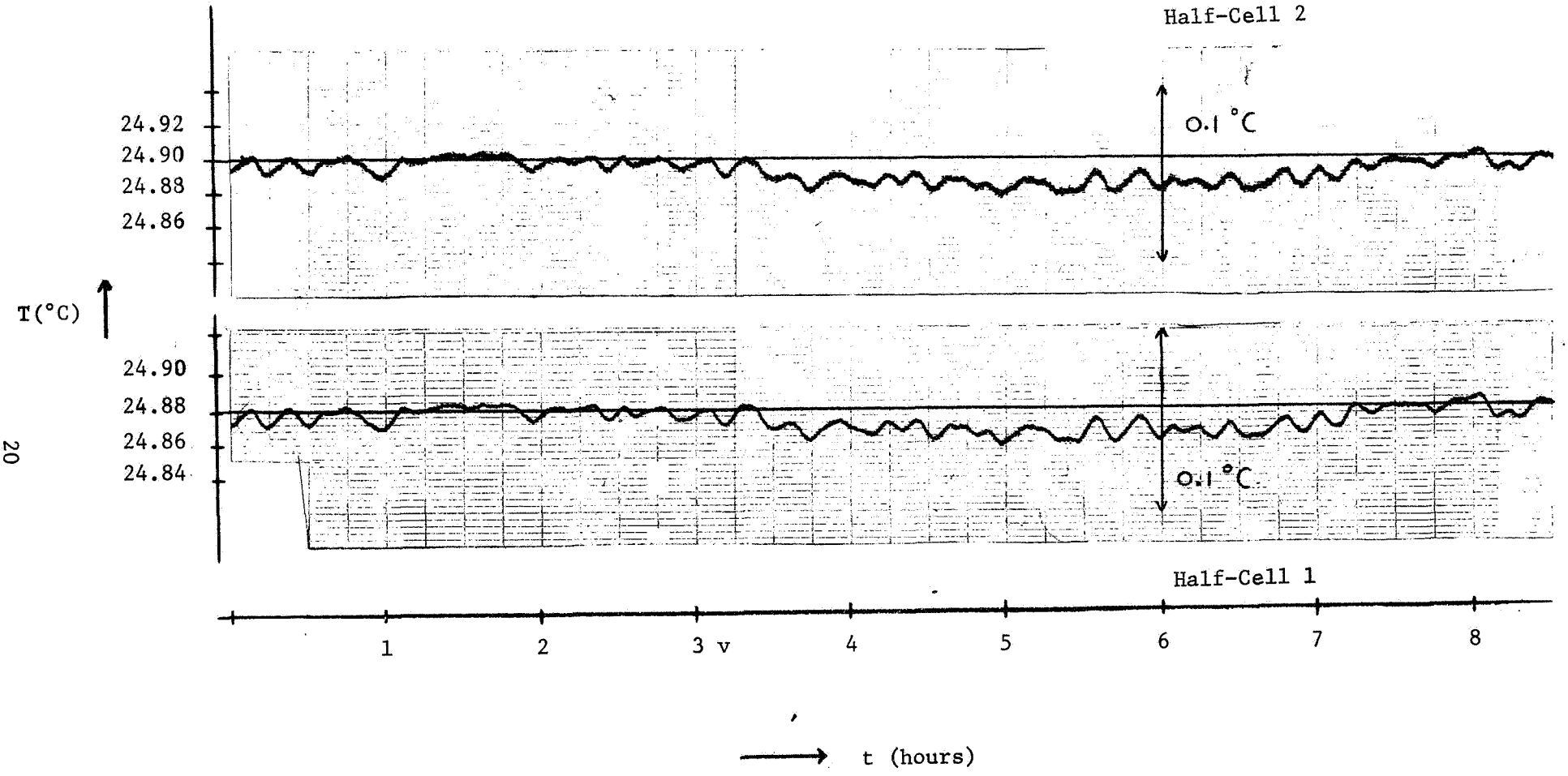

Figure 3.

Performance of Temperature Control:
temperature in two cell compartments recorded together

It was determined that this coating approximately halves the heat transfer rate.

Initially a system was devised and constructed in which the resistance of the thermistors was measured by an A.C. bridge circuit, the bridge unbalance amplified to actuate a relay that opened a solenoid valve to lead cooling water through the coil. However by using cooling water of 20°C it was found that very low flow rates have to be used and that even then serious overcooling occurred. Also the dead span of the "Thermistemp" controller was too large to get narrow control. Therefore the cooling coils were connected to the external circulation circuit of a constant temperature bath (No. 66600, Precision Scientific Corporation, Chicago, Illinois 60647). This bath has long-term temperature stability of better than $\pm$ 0.01°C. By keeping the bath temperature about 0.2°C lower than the required cell temperature, enough heat can be taken up by the cooling coils to obtain a very reasonable long-term and short-term temperature constancy in each cell half. The maximum temperature difference measured between the two cell compartments during an experiment was 0.02°C.

The temperature regulation system as described is able to keep the temperatures of the cell solutions over 24 hour periods between limits of $\pm$ 0.01 at the most for long-term and short-term stability. A typical example is given in Figure 3. In this experiment the inside cell temperature was around 24.90°C, the temperature of the circulation bath was 24.75 $\pm$ 0.01°C and the box was kept at 24.95 $\pm$ 0.1°C. We feel that the performance of the temperature regulation system is adequate for our purposes and that the error caused by the temperature uncertainty especially in the hyperfiltration experiments will be less important than for instance the concentration uncertainty.

II-3. The Concentration Feedback Mechanism

II-3-1. General Description

The concentration feedback mechanism was devised in order to keep the concentration in each of the two cell compartments constant within narrow limits. The system diagram is shown in Figure 4. The resistance of the conductivity cell described in Section II-1-2 is continuously compared to that of a reference resistance by an impedance comparator bridge (Section II-3-2). The output signal of this bridge is amplified, and when the difference between standard and unknown exceeds a presettable value a relay is actuated, which at the donating side starts the motor of an automatic buret filled with a concentrated salt solution, while at the receiving side the relay starts a pump which circulates the cell solution through a mixed-bed demineralizing column at a very slow rate. The electronic and electrical parts of this system have been constructed and tested and are described in detail in the following paragraphs. An example of the performance of the system is presented in Section III.

II-3-2. Impedance Comparators and Amplifiers

When the temperature of the solutions in the reference cell and the transport cells is kept within very narrow limits, the resistance difference is a measure for the concentration difference between the two solutions. An accurate 1605 AH impedance comparator (General Radio Company, West Concord, Massachusetts) is used to compare the two resistances. This instrument measures the difference of the total impedance and the phase angle between an unknown and a standard. The phase angle difference between our conductivity cell and the reference resistance is between 0.01 and 0.03 radians. It can easily be compensated by using a capacitor of the order of 0.01 - 0.04 micro F in parallel with the reference resistance. This

phase angle difference remains constant during an experiment. Differences in total impedance are caused only by the Ohmic parts of the impedance of the conductivity cell.

The impedance comparator has impedance difference ranges of 0.1, 0.3, 1 and 3% full scale. The read-out accuracy is 3% of full scale. This means that by using the lowest scale, resistance differences as low as 0.005% can be detected and measured, approximately equivalent to 0.005% concentration difference between reference and standard solution. For a positive or negative full scale deflection of the total impedance difference meter the comparator gives an output of $\pm$ 60 mV. Since the sensitive relay has a coil resistance of 480 ohm and needs 0.28 ma actuation current, an amplifier has to be used. The input of the amplifier has to be floating because the output of the comparator is at 45 V above ground. Amplifiers of very low drift are necessary. At one side we use a Model 196 amplifier, at the other side a Model 203A electrometer-amplifier (Kintel, San Diego, California). With the amplifiers at gain 30, the relays are actuated when the impedance differences are 5% of the full scale deflection. By using different ranges and different gains any impedance difference between 0.003% and 1% can be used as actuation limit. Special precautions were taken to solve the difficulties caused by the fact that we use two comparators for measuring the resistance of two conductivity cells which are electrically connected via the solutions and the membrane.

First the comparator input is connected to the ground via large blocking capacitors (C_1, C_2 in Figure 4, 20 micro F $\pm$ 5%, Polystyrene) to prevent direct current leaks via conductivity cell 1-ground-conductivity cell 2 in an electroosmosis experiment. These capacitors do not influence the A.C. resistance measurement.

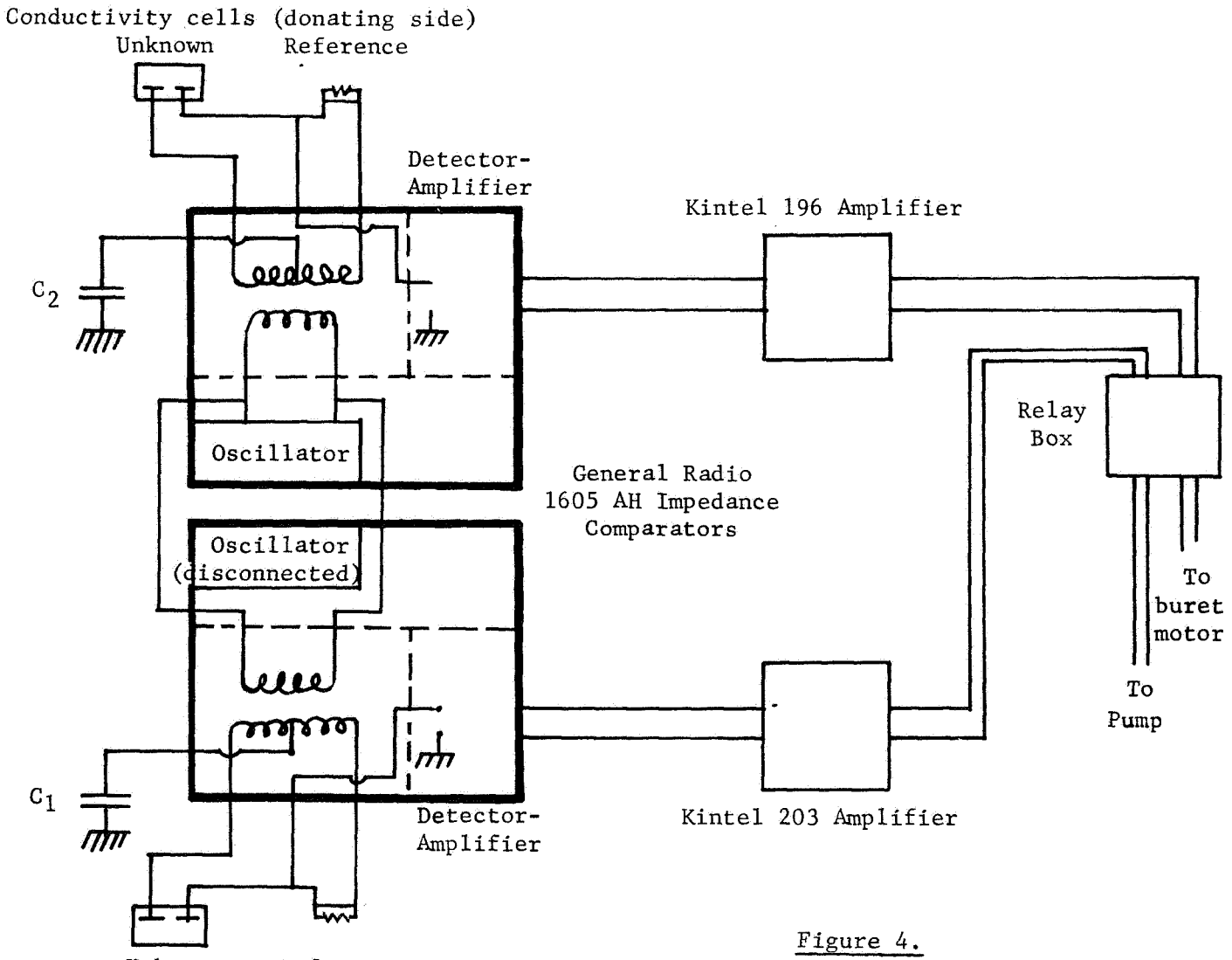

Figure 4.

Concentration Feedback Mechanism

C_1 = 20 μF

Secondly the oscillator of one comparator is internally disconnected and the oscillator of the other comparator is used for excitating both bridge circuits. This is to avoid an alternating loop current that would pass through the bridges via the conductivity cells, the membrane cell solutions and the membrane, the oscillators of the two comparators generally being out of phase.

II-3-3. Relay System.

A polarized relay has to be used for actuation by the amplifier output, so that the solenoid valves or buret motor will be switched on only when the concentration exceeds or falls below a presettable region around the reference concentration in the salt "receiving" and "donating" cell-halves respectively. A polarized relay (MDP 1007, Potter and Brumfield Division, American Machine and Foundry Co., Princeton, Indiana) is used. These D.C. relays have a coil resistance of 480 ohm and need a pull-in current of 0.28 ma. The output is too small to actuate the pump and motor directly; therefore, a second relay (KAP 11 AG, Potter and Brumfield) working on 115 V A.C. is used in series with the first one.

It was found that the sparks between the contact points of the relays at the moment of switching influenced the reading of the comparators, causing an oscillation of the whole system. This was suppressed by connecting 0.1 micro F capacitors parallel to the output contacts of each relay. The diagram for the constructed relay box, which can handle the two signals, is shown in Figure 5.

II-3-4. Demineralizing Column and Metering Buret

At the receiving side of the system a magnetic-drive centrifugal pump, Model 7004 (Cole-Parmer, Chicago, Illinois 60626) is used. The pump

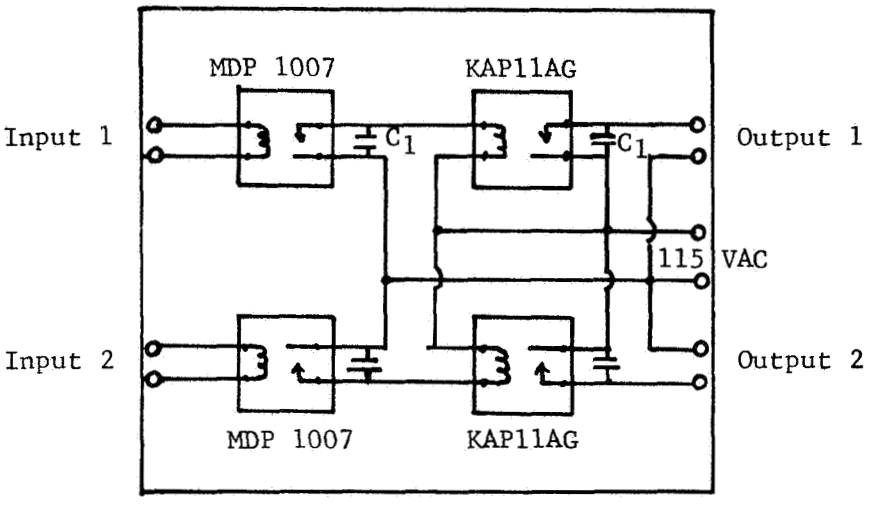

Figure 5.

Relay Box for Two Feedback Systems

C_1 = 0.1 μF Relays: Potter and Brumfield

is run at a very low speed by means of a variable transformer connected to the relay box. A fine, metering needle valve [Type (stainless steel) 4L, Nupro Company, Cleveland, Ohio 44110] is used to regulate the flow through the column and have the same flow velocities in different experiments. This flow velocity is very important for the overshoot in the concentration feedback. Normally, flow rates between 0.2 and 2 ml per minute are used. A diagram of the system is shown in Figure 6. The other valves are Nupro 4 VD "Zytel" valves; all valves have 1/4" "Swagelok" connectors.

Ion exchange columns of different volumes can be inserted, depending on the amount of salt to be transported. In the first electromigration↔ electroosmosis experiment a column volume of 15 ml was used. The connections to the cell are 1/4" hard polyethylene tubing. During an experiment valve 1 (Figure 6) is closed, valve 3 opened and the flow regulated by means of valve 2. The line between valve 2 and the cell is filled with the cell solution before the experiment; all other lines, including the line between valve 3 and the cell, are filled with deionized water. When the experiment is finished, valves 2 and 3 are closed, valve 1 is opened and the liquid in the remaining lines are circulated through the mixed bed resin. For this reason the distance between the metering valve and the "Union T" connection is as small as possible (1/2").

The complete ion exchange system is tested under pressures up to 20 psi. The automatic buret (4-2304A actuator, 4-2312 reservoir, American Instrument Company, Silver Spring, Maryland) has a 30 ml cylindrical glass reservoir, which is filled with a concentrated salt solution. The motor pushes a glass piston into the reservoir and the volume delivered is read

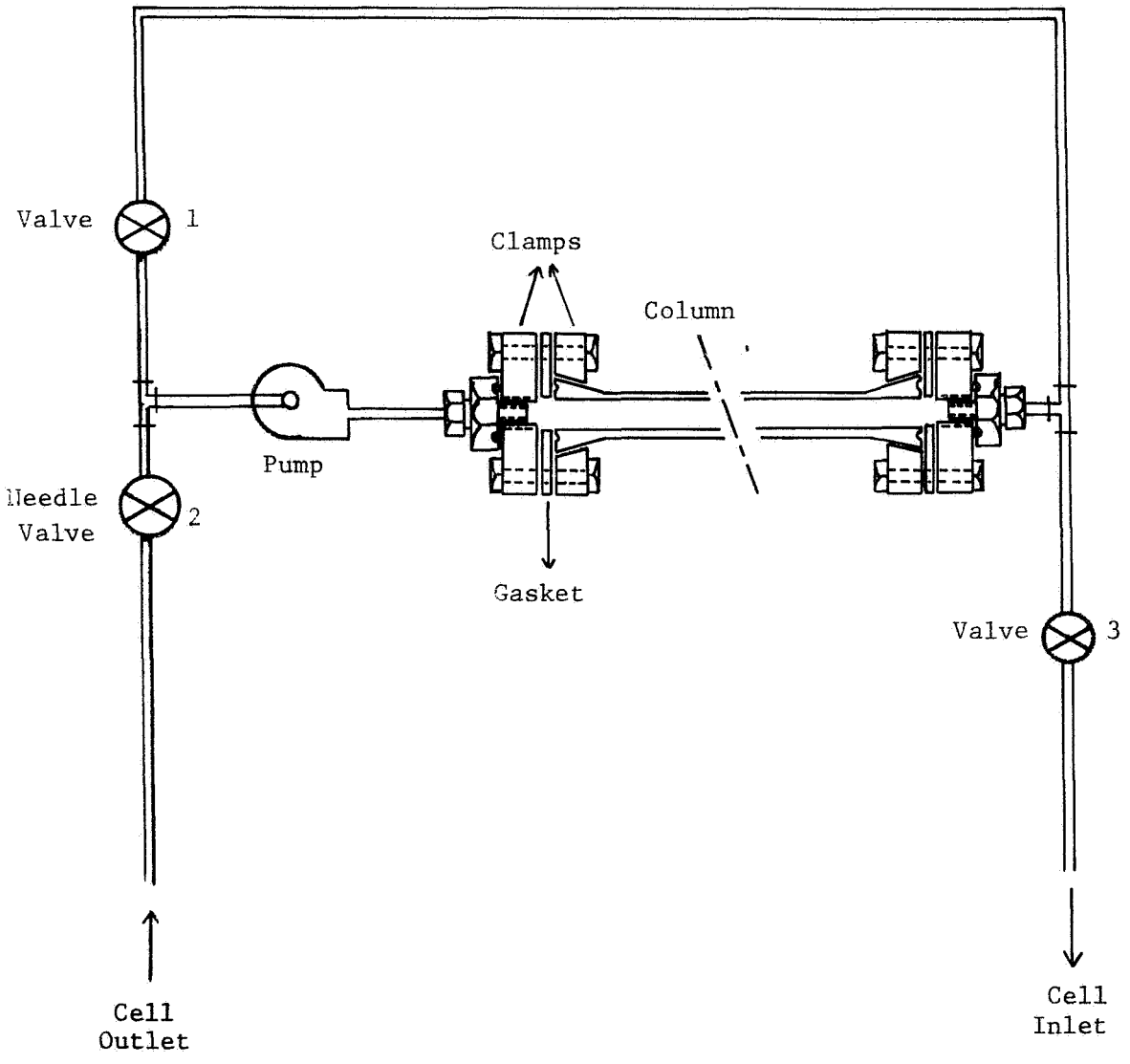

Figure 6. Demineralizing column system

on a calibrated 5 digit dial. The buret has variable speed control, however even at the lowest speed the concentration overshoot was too high. Therefore here too, the relay box is connected to the buret via a variable transformer. The required volume delivery for minimum overshoot depends on the concentrations of the solutions in the cell and the buret reservoir. Normally delivery rates between 2×10^{-3} and 10^{-2} ml of a 1M NaCl solution per minute are used. The buret reservoir has a "Teflon" stopcock at the outlet tip and is connected to the cell with 1/4" hard polyethylene tubing. A stainless steel hypodermic needle in an aluminum housing (Roehr Products Co., Inc., Deland, Florida) is connected to the plastic tubing and fitted into a 1/4" "Swagelok" connector, which is inserted in the bottom of the cell so that no concentrated solution will flow out due to gravity effects. The tip of the hypodermic needle is mounted flush with the inside of the cell wall.

III. Experimental Results

This section deals with the experimental performance of the system, as determined in the preliminary experiments. These preliminary results will only be used as guidelines for future more accurate experiments. Volume and salt flows have been measured in dialysis ↔ osmosis, hyperfiltration and electromigration ↔ electroosmosis experiments. In an electromigration ↔ electroosmosis experiment the apparent salt flow and the volume flow are higher than in the other experiments, (Section I-2); therefore, the results of this type of preliminary experiment are reported in the following.

The experimental procedure is as follows. The cell is assembled with the two Ag/AgCl working electrodes inserted. The two compartments are filled with the NaCl solutions to be used. Then the high concentration (donating) side is connected to the automatic buret and the low concentration (receiving) side to the ion-exchange column system. The cooling coils are connected to the constant-temperature circulation bath. The temperature reaches the desired constant value within about 30 minutes; the current is then started. During the temperature equilibration period the feedback mechanism controlling the concentration is inactivated, by varying the reference resistance. The difference between cell and reference resistance is set at zero as soon as the current is switched on. The salt transport due to dialysis during the temperature equilibration period is very small compared to the subsequent electromigration flux; it can be accounted for if necessary. Cell temperatures, cell-pipet volumes, buret reading, comparator readings and current are regularly recorded. The current is stopped when the concentrations in both compartments show as small a fluctuation as possible from the prescribed values. Final

temperatures and volumes are recorded and the cell solutions are sampled for the concentration determinations.

Table III-1 gives the inital and final values of concentration (in moles per liter) titrated with the same $AgNO_3$ standard solution*, temperature and resistance of the conductivity cells (calculated from the comparator reading), and the total number of moles transported as calculated from equation (4) (Section I-2). A current of 15.0 ma was applied, the membrane area exposed through the holes in the support in 14.6 cm^2. The total salt transport calculated from the donating side can be checked by comparison with the salt taken up by the demineralizing column connected to the depleted side. In this experiment the amount of Cl^- eluted from the column was about 10% lower than the 11.26 mmole transferred from the buret into the donating cell compartment. This was caused by salt still present in the lines due to incomplete circulation after the experiment. The salt held up in the lines was determined separately and the sum of column and line content was within 2% of the value calculated from the buret side.

The performance of the feedback mechanism is seen to be satisfactory. The analytical determinations of initial and final concentrations do not differ significantly. The difference of 0.1% in final and initial cell resistance at the receiving side was caused by a reference resistance adjustment early during the experiment. An example of the concentration feedback cycles is given in Figure 7. It is seen that the feedback system

*This $AgNO_3$ solution is standardized against a NaCl standard (0.1M, $\pm$ 0.1%, P-H Tamm, Altuna, Sweden, distributed by Bio Rad Laboratories, Richmond, California). The same NaCl solution will be used for standardizing all $AgNO_3$ solutions.

Table III-1.

Concentrations, c, Temperature, T, and Salt Transport in an Electromigration ↔ Electroosmosis Experiment

	Donating Side	Receiving Side
$\frac{c\ (initial)}{mole\ NaCl\ cm^{-3} \times 10^3}$	0.2103 ± 0.0003	0.0532 ± 0.0001
$\frac{c\ (final)}{}$	0.2097 ± 0.0003	0.0535 ± 0.0001
$\frac{R\ (initial)}{(Ohm)}$	184.2	719.0
$\frac{R\ (final)}{(Ohm)}$	184.2	719.8
$\frac{c\ (buret)}{mole\ NaCl\ cm^{-3} \times 10^3}$	0.978 ± 0.002	
$\frac{T\ (initial)}{(°C)}$	25.00	24.96
$\frac{T\ (final)}{(°C)}$	25.01	24.96
$\frac{Total\ mole}{transported}$	$(11.26 \pm 0.05) \times 10^{-3}$	
$\frac{\frac{I}{\mathfrak{F}} \cdot t}{(mole)}$	11.29×10^{-3}	

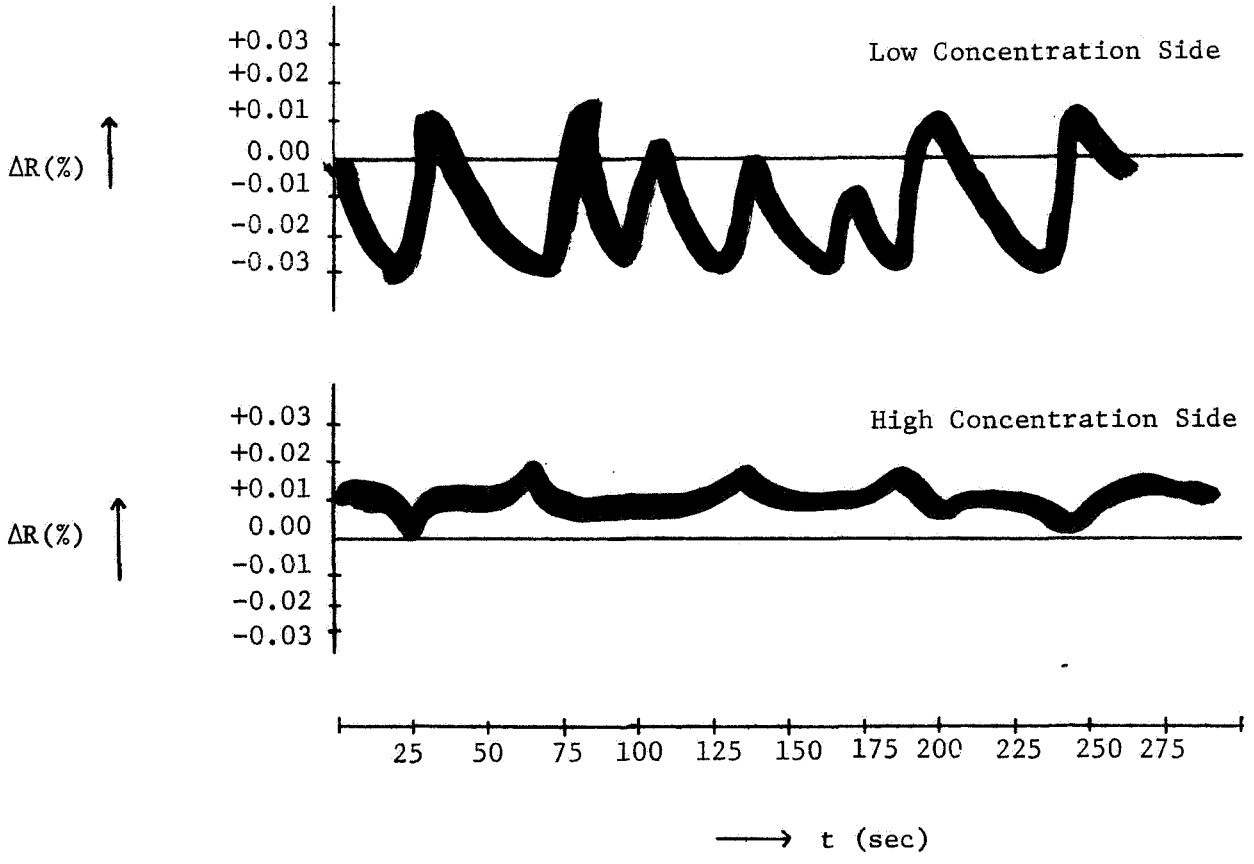

Figure 7. Difference between reference resistance and conductivity cell resistance, ΔR, vs. time, t

in the low-concentration compartment is activated when the cell resistance falls below 0.03% of the initial value determined by the reference resistance (720.0 ohm). The overshoot in the high-concentration compartment was never more than +0.02% and is normally +0.01%. At the buret (high concentration side) the concentration change is more gradual due to the "buffering" effect of the higher concentration; hence a smoother curve is obtained. The buret is activated when the resistance of the concentration cell is about 0.02% more than the reference resistance. There is almost no overshoot to the low-resistance.

In Figure 8 the total salt flow $J_s \cdot A$ (A = membrane area) is plotted vs. time. The duration of the experiment was 20 hours. Each point in Figure 8 is calculated from the buret reading, buret solution concentration, pipet reading and cell solution concentration using equation (4) of Section I-2. The volume change due to mixing of the buret and cell solutions was neglected; in future experiments this effect will be taken into account. The $\Delta v_{app} \times c$ term in equation (4) is about 20% of the $\Delta v_b \times c_b$ term. Also a correction has been made for the difference between initial resistance setting and actual value at the time of reading. Normally this correction is less than 0.01 mmole. The points at 54,600, 56,400, 59,400 and 63,600 seconds represent overshoots of -4.0, -3.1, -2.1 and -0.6 per cent respectively, due to misfunctioning of a relay during a limited period. The deviation of -4.0% at $t = 5.46 \times 10^4$ sec results in a correction on the $J_s \cdot A$ calculated from equation (4) at this time (10.08 mmole) of -1.60 mmole (compartment volume 200 ml, solution concentration 0.2M). For the other points it is less. It is seen from Table III-1 that the apparent total salt transport is very close to the $\frac{I}{\mathcal{F}} \cdot t$ value calculated for an ideally cation-selective

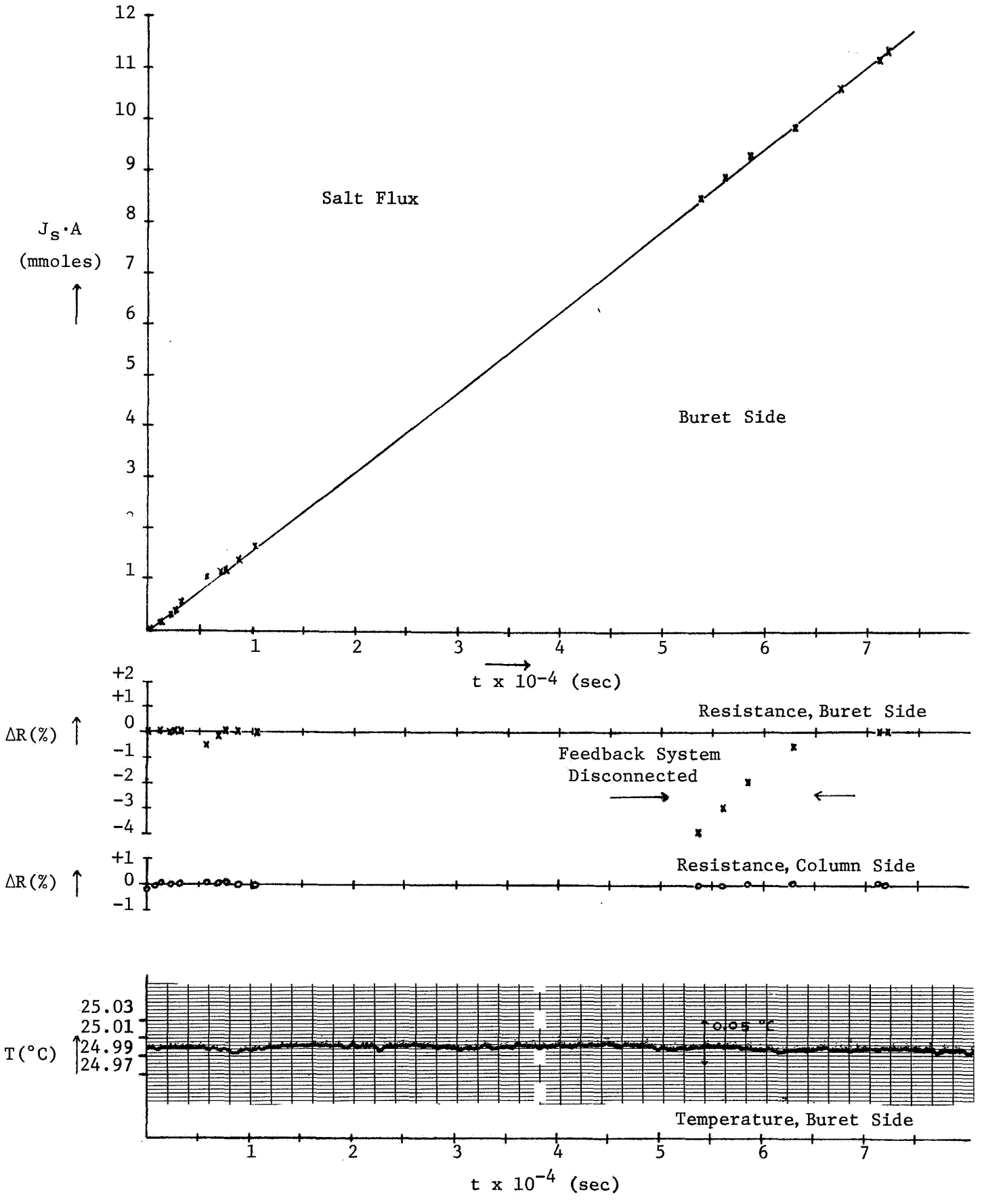

Figure 8. Salt Flux, Resistance Differences and Temperature During an Electromigration ↔ Electroosmosis Experiment

membrane. $J_s \cdot A$ has to be corrected for the diffusion of salt through the membrane. In a dialysis-osmosis experiment an amount of 0.1 mmoles of salt diffused from the high to the low concentration side in 20 hours. Assuming that this diffusion rate is the same in the electromigration experiment, this value has to be subtracted from our total salt transport for the transference number calculations.

It is important to notice that without the feedback mechanism the concentration at the low-concentration side would have risen from about 0.05 to about 0.1 mole per liter, and at the high-concentration side it would have decreased from about 0.21 to about 0.16 mole per liter. The actual concentration was constant within narrow limits (except for the period of relay malfunctioning, when there was a variation of a few percent in the high-concentration compartment). The temperature remained at $25.00 \pm 0.015°C$. Due to difficulties with the pipet system, volume flows in this experiment are not reported. However results from the first hours of the experiment indicate that the volume flow is linear in time and in subsequent experiments volume flows have been determined.

IV. Conclusion

During the first year of this research the emphasis has been on the development and construction of a transport cell, equipped with a concentration feedback system. This system maintains the concentrations in both compartments constant in spite of the transport processes which occur. The conductance of the cell solutions can be held between maximum deviations from the initial state of +0.02% and -0.01% for the donating side and of -0.03% and +0.01% for the receiving side. The temperature in either cell half can be held within $\pm$ 0.01°C of the starting temperature.

Without temperature compensation of the conductance the temperature uncertainty adds $\pm$ 0.02% to the concentration uncertainty. Both the temperature and the conductance difference can be measured more accurately than these limits and corrections for deviations from constancy can be made.

In preliminary experiments the overall performance of the system was shown to meet design specifications.

V. Future Work

Transport experiments will be carried out with AMF C-103 cation exchange membrane. A simple characterization following standard procedures will be made. Dialysis ↔ osmosis, electromigration ↔ electroosmosis, and hyperfiltration experiments will be performed, all with the same concentration difference between the solutions. Dependence of some transport properties, e.g. dialysis coefficient, osmotic flow coefficient and transport numbers on the stirring speed will be determined. The electromigration ↔ electroosmosis experiments will be done at different current densities in order to examine the influence of current density on water transport number, which has led to conflicting data in the literature.[19,6,20,21] Two types of concentration dependence measurements can be done, viz. (a) all measurements can be performed with a carefully chosen series of concentrations in the two cell compartments, and (b) the hyperfiltration and electromigration ↔ electroosmosis experiments can be done at a series of fixed identical concentrations in the two compartments. Finally, we plan to summarize the theory in "readily digestible" form for future use in membrane characterization. The appendix to this report represents a start in this direction.

ACKNOWLEDGEMENT

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Thanks are due to Mrs. D. A. Robinson for editing the manuscript of this report.

APPENDIX

The Transport Equations

Assuming that the difference in molar volume of the species in the two cell solutions is negligible, the fluxes are continuous, and equation (1) yields for the system Na^+ (+), Cl^- (-), H_2O (w):

$$J_w = - L_{ww}(\bar{v}_w \Delta p + \Delta\mu_w) - L_{w+}(\bar{v}_+ \Delta p + \Delta\mu_+^c + \mathcal{F}\Delta\phi) - L_{w-}(\bar{v}_- \Delta p + \Delta\mu_-^c - \mathcal{F}\Delta\phi) \quad \text{(A-1)}$$

$$J_+ = - L_{+w}(\bar{v}_w \Delta p + \Delta\mu_w^c) - L_{++}(\bar{v}_+ \Delta p + \Delta\mu_+^c + \mathcal{F}\Delta\phi) - L_{+-}(\bar{v}_- \Delta p + \Delta\mu_-^c - \mathcal{F}\Delta\phi) \quad \text{(A-2)}$$

$$J_- = - L_{-w}(\bar{v}_w \Delta p + \Delta\mu_w^c) - L_{-+}(\bar{v}_+ \Delta p + \Delta\mu_+^c + \mathcal{F}\Delta\phi) - L_{--}(\bar{v}_- \Delta p + \Delta\mu_-^c - \mathcal{F}\Delta\phi) \quad \text{(A-3)}$$

In these equations $\Delta\phi$ is the electrical potential difference in the solution between the two solutions at either side of the membrane. The significance of the separation of the total electrochemical potential $\tilde{\mu}_i$ in a concentration part μ_i^c and an electrical part $z_i\mathcal{F}\phi$ has been the subject of considerable discussion.[22] In fact only an electrode potential is thermodynamically defined. Also the experimentally controllable parameters are Δp, $\Delta\mu_s^c$ ($\Delta\mu_s^c \equiv \Delta\mu_+^c + \Delta\mu_-^c$) and i (rather than the potential). Duncan[12] transforms equation (A-1) to a system in which the quantities to be measured experimentally are expressed as a linear combination of Δp, $\Delta\mu_s^c$ and i. To do this the following transformations have to be made:

1) $$\Delta\mu_w = - \frac{c_s}{c_w} \Delta\mu_s \quad \text{(A-4)}$$

This is an integrated form of the Gibbs-Duhem relation.

2) $$\Delta\mu_+^c + \Delta\mu_-^c = \Delta\mu_s^c \quad \text{(A-5)}$$

3) $$\mathcal{F}\Delta\phi = \mathcal{F}\Delta\phi_- + \Delta\mu_-^c \quad \text{(A-6)}$$

Where $\Delta\phi_-$ is the potential difference measured between two Ag/AgCl electrodes.

When equations (A-4), (A-5) and (A-6) are substituted in equations (A-1), (A-2), (A-3), it is found that the following transformation for the fluxes has to be made in order to preserve reciprocity:

$$J_V = \bar{v}_w J_w + \bar{v}_+ J_+ + \bar{v}_- J_- \tag{A-7}$$

$$J_D \equiv J_s - \frac{c_s}{c_w} J_w \tag{A-8}$$

$$i/\mathcal{F} = J_+ - J_- \tag{A-9}$$

With anion-reversible working electrodes, the flux of the cation J_+ is equal to the apparent salt flux J_s:

$$J_+ = J_s \tag{A-10}$$

The following expressions are obtained for J_V, J_D, and i:

$$J_V = - L_{VV} \Delta p - L_{VD} \Delta\mu_s - L_{VE} \mathcal{F}\Delta\phi_- \tag{A-11}$$

$$J_D = - L_{DV} \Delta p - L_{DD} \Delta\mu_s - L_{DE} \mathcal{F}\Delta\phi_- \tag{A-12}$$

$$i = - L_{EV} \Delta p - L_{ED} \Delta\mu_s - L_{EE} \mathcal{F}\Delta\phi_- \tag{A-13}$$

with:

$$L_{VD} = L_{DV}, \quad L_{VE} = L_{EV}, \quad L_{DE} = L_{ED} \tag{A-14}$$

If now the electric current i is substituted for $\Delta\phi_-$, using equation (A-13) Duncan's final set is obtained:

$$J_V = - \Delta p \left(L_{VV} - \frac{L_{VE}\, L_{EV}}{L_{EE}} \right) - \Delta\mu_s \left(L_{VD} - \frac{L_{VE}\, L_{ED}}{L_{EE}} \right) + i \cdot \frac{L_{VE}}{L_{EE}} \tag{A-15}$$

$$J_D = - \Delta p \left(L_{DV} - \frac{L_{DE}\, L_{EV}}{L_{EE}} \right) - \Delta\mu_s \left(L_{DD} - \frac{L_{DE}\, L_{ED}}{L_{EE}} \right) + i \cdot \frac{L_{DE}}{L_{EE}} \tag{A-16}$$

$$- \mathcal{F}\Delta\phi_- = + \Delta p \frac{L_{EV}}{L_{EE}} + \Delta\mu_s \cdot \frac{L_{ED}}{L_{EE}} + i \cdot \frac{1}{L_{EE}} \tag{A-17}$$

It is seen that in these transformations reciprocity is maintained.

Thus the flow equations for J_w, J_+ and J_- can be transformed into a very useful set which is closely related to quantities measured directly in a transport experiment for which the Onsager relations still hold. However in systems with a concentration gradient, the use of the Gibbs-Duhem relation in an integrated form [equation (A-4)] and the definition of the "salt-water" separation flow J_D [equation (A-8)] lead to ambiguities not present when the less easily applicable but exact original set (A-1), (A-2), (A-3) is used.

Even if an integration of the Gibbs-Duhem equation:

$$c_w \text{ grad } \mu_w + c_s \text{ grad } \mu_s = 0$$

can be made a suitable average, value of $\frac{c_s}{c_w}$ has to be chosen for insertion in equation (A-4). The same holds for J_D, and in general J_D (as J_V) will not be a conserved quantity along the diffusion profile.

The "transport number" of Duncan is often called "transference number of the positive ion".[23] It can be expressed in terms of the L coefficients of equations (A-11), (A-12) and (A-13) by use of equation (A-16):

$$t \equiv \left(\frac{\mathcal{F} J_D}{i}\right)_{\Delta p=0,\ \Delta\mu=0} = \frac{L_{DE}}{L_{EE}} \qquad \text{(A-18)}$$

It is seen from equation (A-17) that t is directly related to the cell potential by:

$$-\mathcal{F}\left(\Delta\phi_-\right)_{\Delta p=0,\ i=0} = t\Delta\mu_s \qquad \text{(A-19)}$$

because $L_{DE} = L_{ED}$. Thus Duncan's number is recognized as the "apparent transport number"[2] found from membrane potential measurements.

Customarily "true transference numbers":

$$t_+ = \left(\frac{\mathcal{F} J_s}{i}\right)_{\Delta p=0,\ \Delta\mu_s=0}, \qquad t_w = \left(\frac{\mathcal{F} J_w}{i}\right)_{\Delta p=0,\ \Delta\mu_s=0}$$

are used.[22] Here J_s and J_w are fluxes relative to an inert component, in our case the membrane.

Expressing J_D [equation (A-8)] in terms of these definitions, we obtain from equation (A-16):

$$\frac{t_+}{\mathcal{F}} - \frac{c_s}{c_w}\frac{t_w}{\mathcal{F}} = \frac{L_{DE}}{L_{EE}} \qquad \text{(A-20)}$$

Where again a suitable average value of $\frac{c_s}{c_w}$ has to be calculated. We can also write Duncan's equations (A-15), (A-16) and (A-17) in the differential form, i.e. starting from gradients rather than finite differences and integrate using the "true transference numbers" to obtain:

$$-\mathcal{F}\Delta\phi_- = \int_1^2 \left(t_+ - \frac{c_s}{c_w} t_w\right) d\mu_s \qquad \text{(A-21)}$$

This relation has been used frequently and can also be derived from Scatchard's equation for the membrane potential.[23] It is seen that the "transference number" t, as obtained from electric potential measurements [equation (A-19)] contains contributions from ion and solvent transference. Its absolute magnitude is therefore smaller than the "true transference number" of the positive ions, t_+, defined as the fraction of the electric current carried by the positive ions.[23]

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LIST OF SYMBOLS

A (cm^2)	effective surface area of membrane
c (mole cm^{-3})	concentration
d (cm)	membrane thickness
f	correction factor for volume change on mixing
g	shrinkage factor of resin
i (amp cm^{-2})	electric current density
I (amp)	electric current
J_i (mole cm^{-2} sec^{-1})	flux of component i
J_V (cm sec^{-1})	volume flux
L_{ij} ($mole^2$ $joule^{-1}$ cm^{-1} sec^{-1})	admittance coefficient
$n_{I.E.}$	number of moles of salt taken up by ion exchange column
p (joule cm^{-3})	pressure
t (sec)	time
t_i	transference number of component i, relative to the membrane. $t_i = J_i \cdot \frac{\mathscr{F}}{i}$
$\bar{v}_j$ (cm^3 $mole^{-1}$)	partial molar volume of component j
Δv_{app} (cm^3) = $v_{final} - v_{initial}$	volume change in pipet during experiment
Δv_b (cm^3)	volume pushed in by buret
Δv_e (cm^3)	volume change due to electrode reaction
X_{ij} (joule sec $mole^{-1}$ cm^{-2})	friction coefficient
z_j	charge number of component j
$\mathscr{F}$ (coulomb $mole^{-1}$)	Faraday's constant
ϕ (volt)	electric potential
$\Delta\phi_-$ (volt)	potential difference between two anion reversible electrodes

π (joule cm^{-3})	osmotic pressure, $\pi = -\frac{\mu_{H_2O}(c) - \mu_{H_2O}(0)}{\bar{v}_{H_2O}}$
$\tilde{\mu}_j$ (joule $mole^{-1}$)	total electrochemical potential of component j
μ_j^c (joule $mole^{-1}$)	concentration part of chemical potential of component j